ORTHO-PARA MIXING INTERACTION IN THE VINYL RADICAL DETECTED BY MILLIMETER-WAVE SPECTROSCOPY AND PREDICTION OF FAST *ORTHO-PARA* CONVERSION RATE

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Ortho-para mixing interaction due to the coupling of nuclear and electron spins was detected for the first time by millimeter-wave spectroscopy of deuterated vinyl radicals, H_2CCD and D_2CCD, of which the ground states are split by the tunneling motion of the α deuteron into two components 0^+ and 0^-, whose separations have been determined to be $\Delta E_0 = 1186.644(16)$ and $771.978(18)$ MHz, respectively. The observed tunneling-rotation spectra are significantly perturbed by the *othro-para* mixing interaction expressed by $\langle 0^\pm | H' | 0^\mp \rangle = (\delta a_F^{(\beta)}/2) \mathbf{S} \cdot (\mathbf{I}_{\beta 1} - \mathbf{I}_{\beta 2})$, where $\mathbf{I}_{\beta 1}$ and $\mathbf{I}_{\beta 2}$ are spins of the two hydrogen nuclei in the β position and $\mathbf{S}$ is the electron spin, which connects rotational levels in the 0^+ and 0^- states, one being an *ortho* level and the other a *para* level. The $\delta a_F^{(\beta)}$ constants for H_2CCD and D_2CCD have been determined to be 68.06(53) and 10.63(94) MHz, respectively, consistent each other within the isotopic mass relation. The *othro* and *para* states are mixed by about 0.097% and 0.0123% due to this interaction. [a] The δa_F constant for H_2CCH should be similar to that for H_2CCD because of the same probability density of the unpaired electron at the β protons, but could not be determined independently in our previous study. It is because the mixing of *para*- and *ortho*-levels of about 0.00044% is much smaller than that for H_2CCD due to the large tunneling splitting of $\Delta E_0 = 16271.8429(59)$ MHz. [b]
The rate constant of *para* to *ortho* ($I_\beta = 0 \to 1$) conversion is predicted as 1.2×10^5 s^{-1} $torr^{-1}$ for H_2CCD, suggesting extremely rapid mutual conversion between *ortho* and *para* nuclear spin isomers of H_2CCD, which is more than 10^6 times faster compared with that in closed shell molecules such as H_2CO and H_2CCH_2.

[a] K. Tanaka, M. Hayashi, M. Ohtsuki, K. Harada, T. Tanaka, *J. Chem. Phys.* **131,** 111101 (2009).

[b] K. Tanaka, M. Toshimitsu, K. Harada, T. Tanaka, *J. Chem. Phys.* **120,** 3604 (2004).